

# PATENT SPECIFICATION

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ASAI and KOSHIRO MORI



## (54) LIQUID CRYSTAL DISPLAY MATERIAL AND A DEVICE INCORPORATING SAME

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD. a corpora-  
tion organized under the laws of Japan, of 1006, Oaza Kadoma, Kadoma-shi, Osaka,  
Japan, do hereby declare the invention, for which we pray that a patent may be  
granted to us, and the method by which it is to be performed, to be particularly  
described in and by the following statement:—

The present invention relates to a liquid crystal display material and a device  
incorporating same.

In liquid crystal display devices which use conventional nematic liquid crystal  
material, slight scattering of light occurs when no voltage is applied across the  
material, and this phenomenon appears as a "haze".

This light scattering occurs at the interfaces of domains formed by the nematic  
liquid crystal molecules, which domains are randomly orientated relative to each other.

A state where no "haze" is present can be created by orientating substantially all  
the liquid crystal molecules perpendicular to a surface which encloses the liquid crystal  
material or parallel with said surface. In the former case, the liquid crystal structure is  
called the homeotropic structure and in case of the latter, the structure is termed  
homogeneous.

The development of the homeotropic structure is influenced by the condition of  
the surface of a substrate in contact with the liquid crystal material.

Known nematic liquid crystal materials do not have molecular orientation strong  
enough to bring about the homeotropic orientation with all substrate surfaces.

This is one cause for the "haze" which usually occurs in liquid crystal display  
devices.

For forming the homeotropic structure, there have been two methods, namely,  
treatment of the surface of a substrate plate and addition of compounds capable of  
controlling molecular orientation. Examples of these methods are as follows:

- (1) Method which comprises adding to the nematic material additives capable of  
controlling the molecular orientation thereof. (For example, dodecyltrimethyl  
ammonium bromide, cetyl esters of gallic acid, etc. are added.)
- (2) Method which comprises coating lecithin and the like on a glass substrate  
plate.
- (3) Method which comprises treating the surface of glass substrate plate with a  
dichromic acid and sulfuric acid mixed solution, hydrofluoric acid, etc.

- (4) Method which comprises providing evaporated film of a metal oxide, a metal fluoride, etc. on a glass substrate plate.

According to the surface treatments such as treatment of the method (3) and formation of the evaporated film of the method (4), it is difficult to orientate strongly the liquid crystal molecules homeotropically and even if the homeotropic structure is formed, it has low stability. On the other hand, when additives capable of controlling the molecular orientation are added as in the method (1) and the surface treatment of method (2), homeotropic structure of high stability can be obtained.

As the additives capable of controlling the molecular orientation, substances having a specific molecular type are chosen.

In this instance, there are two alternatives depending upon the surface of substrate plate. According to one of them, the homeotropic structure is formed with any untreated surface and according to the other of them, a homeotropic structure having a high stability is formed in contact with a treated polar surface.

These additives characteristically have a long alkyl chain and a polar group for adsorption on to the surface at one end of the molecule.

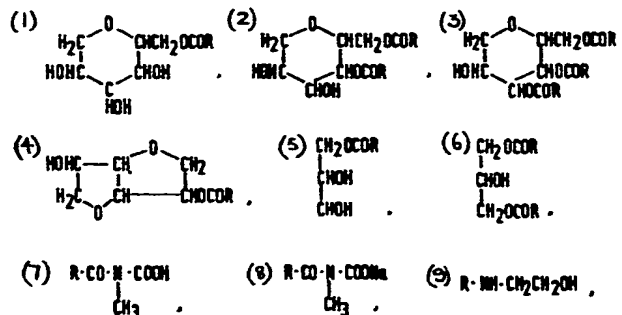
The polar group of these additives is preferentially adsorbed on to the surface which encloses the liquid crystal to form an adsorbed molecularly-orientated monolayer. This monolayer imparts a perpendicular orientation to the adjacent layer of liquid crystal molecules. The liquid crystal molecules are kept parallel with each other by intermolecular interaction with the long alkyl chains of the adsorbed layer and as the result the liquid crystal molecules are made stably perpendicular to the interface. As the terminal polar group, a hydroxyl group, carboxyl group, carbonyl group, quaternarized nitrogen atom, sulfonic acid group or phosphoric acid group may be chosen for example. At least one terminal polar group should be present. When at least one polar terminal group is connected directly to a cyclic hydrocarbon nucleus the perpendicular orientation is easily brought about or becomes stable.

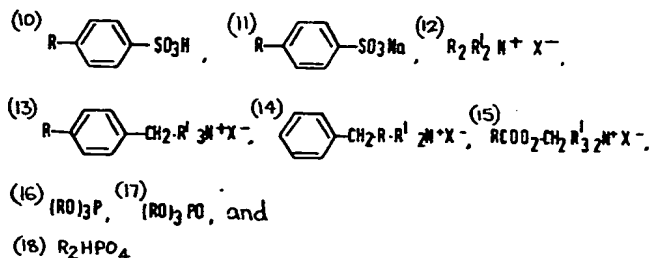
In general, a liquid crystal display device comprises flat glass plates on either side of a liquid crystal layer. Electrode material such as a transparent metal oxide or a reflective metal is placed on the surface of each said glass plate.

These flat glass plates are usually kept parallel to each other and spaced by an extremely narrow interval of several  $\mu$  to several ten  $\mu$  and they are required to be highly planar. For this purpose, float glasses are used or the surface of a glass substrate is optically polished. Some of the polishing procedures result in local scratches having a certain direction on the glass plate, due to which the orientation of the liquid crystal molecules is locally disturbed. After all, the liquid crystal composition is in contact with the surfaces of the substrate plates which enclose said composition and the surfaces of the electrode material on the substrate plates. In general, liquid crystal molecules placed on the polar surface of the electrode material are apt to become perpendicularly oriented, but conventionally it has been difficult to produce a uniform homeotropic orientation on the surface of the glass substrate plate because it depends upon the precise treatment each part has locally received. This difficulty may arise even when compounds capable of controlling the orientation of molecules are added.

Such being the case, it has been difficult to obtain a liquid crystal display device having no "haze" across its whole area.

The present invention provides a liquid crystal display material comprising a nematic liquid crystal material and at least one additive selected from types of compounds having the following general formulae:





wherein R in formulae (1)—(16) is selected from alkyl groups of 10—24 carbon atoms and an oleyl group, R in the formulae (17) and (18) is selected from methyl and ethyl groups and X<sup>-</sup> is a monovalent anion.

These compounds are capable of controlling the orientation of liquid crystal molecules.

The present invention also provides a liquid crystal display device incorporating the liquid crystal display material of this invention, as defined above, said material being interposed between two glass substrate plates, the internal surface of each plate being covered at least in part with a thin film electrode at least one electrode being transparent and any remaining internal plate surface having no electrode being subjected to chemical cleaning treatment or being provided with an electrically insulating vacuum evaporated film.

The extent to which these additives affect the orientation is illustrated by the following experimental Example.

In the accompanying drawings:—Fig. 1 shows the state obtained when a liquid crystal material according to the invention was inserted between enclosing plates whose surfaces were untreated.

Figs. 2 and 3 are illustrations of a liquid crystal display device obtained using the present invention.

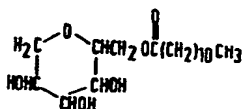
As shown in Fig. 1, an indium oxide vacuum evaporated film 2 was provided on each of two optically polished glass substrate plates 1. The plates were kept parallel to each other at an interval of 10  $\mu$ , between which a composition comprising the following nematic liquid crystal containing about 1% by weight of one of the additives enumerated below was inserted and the state of the composition was observed.

As the nematic liquid crystal, a mixture of *p*-anisylidene-*p*-*n*-heptylaniline, *p*-ethoxybenzylidene-*p*-*n*-butylaniline and *p*-*n*-propoxybenzylidene-*p*-*n*-pentylaniline in equal weight ratio was used.

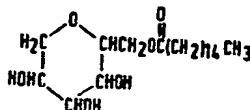
The additives incorporated were as follows:

[A] Sorbitan compounds

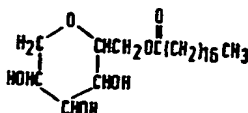
(1) Sorbitan monolaurate



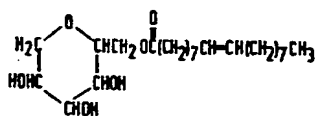
(2) Sorbitan monopalmitate



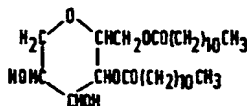
(3) Sorbitan monostearate



## (4) Sorbitan monooleate



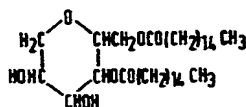
## (5) Sorbitan dilaurate



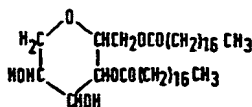
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## (6) Sorbitan dipalmitate

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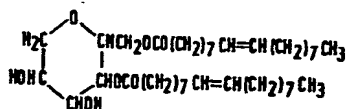


## (7) Sorbitan distearate



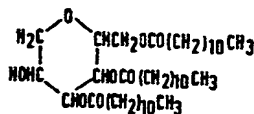
## (8) Sorbitan dioleate

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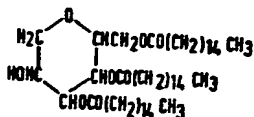


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## (9) Sorbitan trilaurate



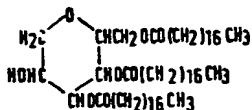
## (10) Sorbitan tripalmitate



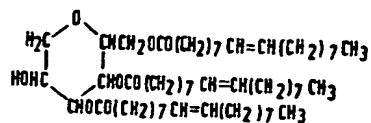
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## (11) Sorbitan tristearate

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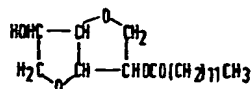


## (12) Sorbitan trioleate



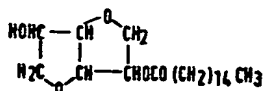
[B] Sorbide compounds  
 (1) Sorbide monolaurate

5

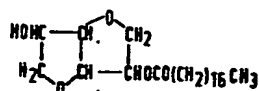


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## (2) Sorbide monopalmitate



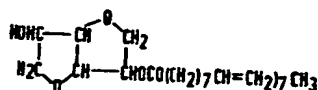
## (3) Sorbide monostearate



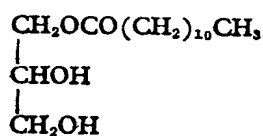
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## (4) Sorbide monooleate

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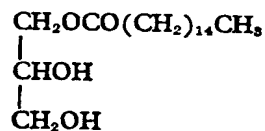
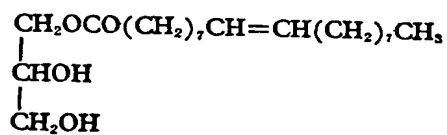
[C] Glycerol ester compounds  
 (1) Glycerol- $\alpha$ -monolaurate

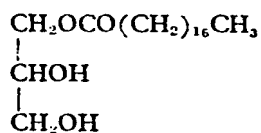
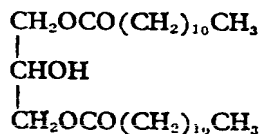


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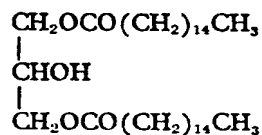
(2) Glycerol- $\alpha$ -monopalmitate

15

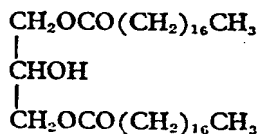
(3) Glycerol- $\alpha$ -monooleate

(4) Glycerol- $\alpha$ -monostearate(5) Glycerol- $\alpha,\alpha'$ -dilaurate

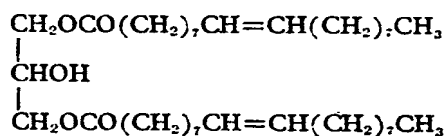
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(6) Glycerol- $\alpha,\alpha'$ -dipalmitate

5

(7) Glycerol- $\alpha,\alpha'$ -distearate(8) Glycerol- $\alpha,\alpha'$ -dioleate

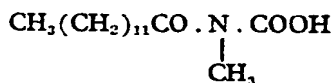
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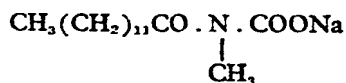
## [D] N-acyl sarcosine compounds

## (1) N-lauroylsarcosine



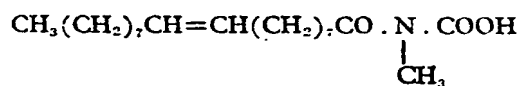
## (2) N-lauroylsarcosine sodium salt

15



15

## (3) N-Oleoylsarcosine



## [E] Oxyethylenealkylamine compounds

## (1) Hydroxyethylenedodecylamine

20



20

(2) Hydroxyethylenehexadecylamine



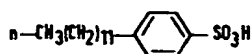
(3) Hydroxyethyleneoctadecylamine



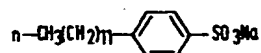
5 [F] Alkylbenzenesulfonic acid compounds

(1) Normal dodecylbenzenesulfonic acid

5

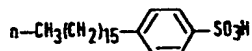


(2) Normal sodium dodecylbenzenesulfonate

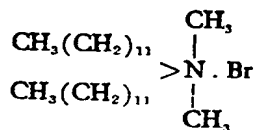


10 (3) Normal cetylbenzenesulfonic acid

10

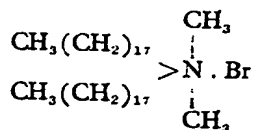


[G] Quaternary ammonium salt compounds  
(1) Didodecyldimethyl ammonium bromide

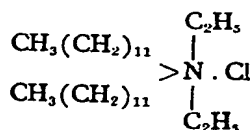


15 (2) Dioctadecyldimethyl ammonium bromide

15

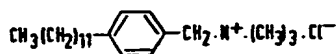


(3) Didodecyldiethyl ammonium chloride



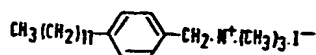
(4) Laurylbenzyltrimethyl ammonium chloride

20

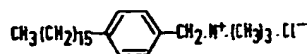


(5) Laurylbenzyl trimethyl ammonium iodide.

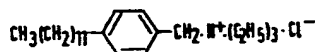
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## (6) Cetylbenzyltrimethyl ammonium chloride



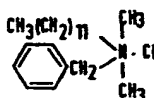
## (7) Laurylbenzyltriethyl ammonium chloride



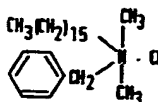
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## (8) Lauryldimethylbenzyl ammonium chloride

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## (9) Cetyldimethylbenzyl ammonium chloride



## (10) Lauroylcholine chloride

10



10

## (11) Palmitoylcholine chloride



## (12) Stearoylcholine chloride



15

## (13) Lauroylcholine iodide

15



## (14) Palmitoylcholine iodide



## (15) Stearoylcholine iodide

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20

## [H] Phosphorus and phosphoric acid compounds

## (1) Tridecyl phosphite



## (2) Trilauryl phosphite

25



25

## (3) Tristearyl phosphite





	(4) Trioctyl phosphate	
	$(\text{CH}_3(\text{CH}_2)_7\text{O})_3\text{PO}$	
	(5) Tridecyl phosphate	
	$(\text{CH}_3(\text{CH}_2)_9\text{O})_3\text{PO}$	
5	(6) Tridodecyl phosphate	5
	$(\text{CH}_3(\text{CH}_2)_{11}\text{O})_3\text{PO}$	
	(7) Tristearyl phosphate	
	$(\text{CH}_3(\text{CH}_2)_{17}\text{O})_3\text{PO}$	
	(8) Dioctyl phosphate	
10	$(\text{CH}_3(\text{CH}_2)_7)_2\text{HPO}_4$	10
	(9) Didecyl phosphate	
	$(\text{CH}_3(\text{CH}_2)_9)_2\text{HPO}_4$	
	(10) Didodecyl phosphate	
	$(\text{CH}_3(\text{CH}_2)_{11})_2\text{HPO}_4$	
15	(11) Dihexadecyl phosphate	15
	$(\text{CH}_3(\text{CH}_2)_{15})_2\text{HPO}_4$	

20 In each case, liquid crystal layer 3 enclosed by the glass substrate plates had "haze" while liquid crystal layer 4 enclosed by the electrode materials had no "haze" and was transparent. When a pair of parallel polarizers were provided before and behind the liquid crystal panel in such a state that the polarizing directions were crossed, the liquid crystal layer 3 appeared light and the liquid crystal layer 4 appeared dark.

25 From the above result, it is confirmed that the liquid crystal 4 interposed between the electrode materials had a homeotropic structure.

As is clear from the results of the above experiment, a liquid crystal display plate showing no "haze" could be obtained when it was composed of only the liquid crystal layer interposed between the electrode materials.

30 In the above Example, explanation has been given with reference to the use of a nematic liquid crystal composition which comprised a nematic liquid crystal containing one of the additives enumerated above. However, the same effect as obtained above could also be attained when at least two of the above additives were incorporated into the nematic liquid crystal.

"Haze" on the surface of the glass substrate plate could not be removed even by increasing the amount of said additives incorporated.

35 The following means may be employed to provide a liquid crystal display plate having no "haze" in the liquid crystal layer contacting the glass surface. That is, a thin film transparent electrode or a thin film metal electrode is provided on each of the opposite surfaces of the two glass substrates and the remaining surface other than that occupied by said electrode is subjected to chemical cleaning treatment or coated with an electrically insulating vacuum evaporated film. Between these two glass substrate plates is interposed a nematic liquid crystal composition containing at least one of the above enumerated additives to obtain a liquid crystal display device.

40 Examples of thin film transparent electrode materials are metal oxides such as oxides of tin, titanium, indium cadmium, etc. (the oxides being doped where necessary, to render them conductive) and examples of the metal electrodes are those of Al, Ni, Pd, Ag, Au, etc.

45 The invention will now be further illustrated in the following Examples.

## Example 1.

Each of two glass substrate plates 1, optically polished and provided with a tin oxide electroconductive thin film 2 on the surface as shown in Fig. 2, was dipped in a mixed cleaning solution of dichromic anhydride and sulfuric acid for one minute.

A nematic liquid crystal material containing any of the additives enumerated above with respect to the device of Fig. 1 was interposed in a container composed of said two treated glass plates which were positioned at an interval of 10 microns. The nematic liquid crystal material used was the same as that used in the device of Fig. 1.

In Fig. 2, a portion 7 of the liquid crystal layer was interposed between glass substrate plate surfaces 5 which were chemically cleaned and a portion 8 of the liquid crystal layer was interposed between electrode material surfaces 6.

Regardless of the kind of additives used, the portions 7 and 8 had no "haze" and were homogeneously transparent.

When this liquid crystal panel was placed between crossed linear polarizers and said panel was rotated, the transmitted light appeared homogeneously dark. This is due to the formation of the homeotropic structure at least partly caused by the additives used in the present invention.

## Example 2.

The same liquid crystal composition as used in Example 1 was interposed between two glass plates, the surfaces of which was covered with electrically insulating vacuum evaporated film 9 of magnesium fluoride, on which an indium oxide vacuum evaporated film 10 was further provided as shown in Fig. 3.

In this case, liquid crystal layer portion 11 was interposed between the surfaces of the magnesium fluoride vacuum evaporated film and liquid crystal layer portion 12 was interposed between the surfaces of indium oxide electrode material.

As in Example 1, the whole layer in this liquid crystal panel also had no "haze" and was transparent regardless of which additive was present in the liquid crystal material. Application of polarizers brought about the same results as those of Example 1 and the whole of the liquid crystal layer had the homeotropic structure.

Other suitable materials for said electrically insulating thin film are those of silicon oxide, aluminum oxide, barium oxide, beryllium oxide, bismuth oxide, magnesium oxide, nickel oxide, antimony oxide, tellurium oxide, thorium oxide, zinc oxide, indium oxide, tin oxide, etc.

## Example 3.

In this Example, other nematic liquid crystal compositions than those used in Examples 1 and 2 were examined to obtain the same results as those in Examples 1 and 2 and the homeotropic structure was also formed due to the additives. Typical examples of the other nematic materials were *p*-anisylidene-*p*-aminophenylacetate, *p*-anisylidene-*p*-aminobenzonitrile, *p*-azoxyanisole, *p*-ethoxy-*p*'-*n*-hexanoyloxy azobenzene and *p*-*n*-hexylbenzoic acid-*p*'-*n*-hexyloxyphenyl esters.

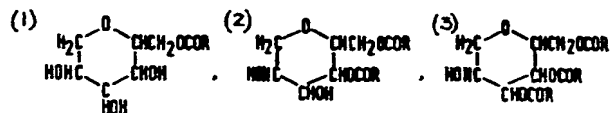
Even when a small amount of an additive for controlling molecular orientation, such as gallic acid cetyl esters and lecithin, (said small amount being such that as would produce "haze" on the surface of a normal glass plate) is added to the liquid crystal material of the present invention, a liquid crystal display device in which no "haze" was present at the surface of the glass plate could be obtained by the aforesaid prior treatment, i.e. chemical cleaning or provision of an electrically insulating vacuum evaporated film.

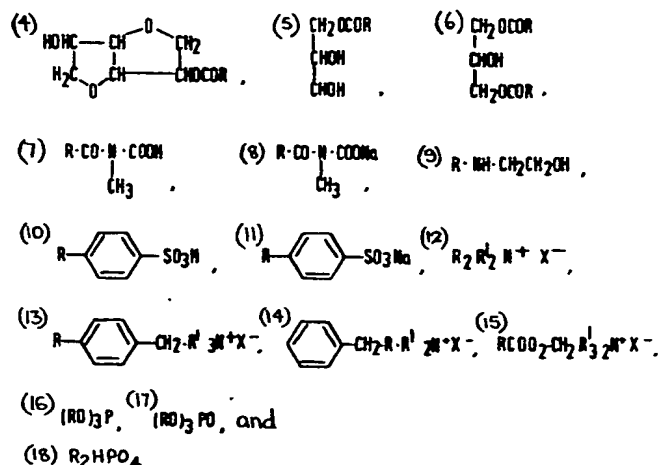
Other additives could be further added in such an amount as not to damage the homeotropic structure to improve other characteristics such as electrical resistance, time constant, contrast, and life.

Liquid crystal devices exhibiting no "haze" possess useful electro-optical effects for display purposes.

## WHAT WE CLAIM IS:—

1. A liquid crystal display material comprising a nematic liquid crystal material and at least one additive selected from types of compound having the following general formulae:





wherein R in the formulae (1)–(16) is selected from alkyl groups of 10–24 carbon atoms and an oleyl group, R in the formulae (17) and (18) is selected from alkyl groups of 4–24 carbon atoms, R' is a methyl or ethyl group and X<sup>-</sup> is a monovalent anion.

2. A liquid crystal display material according to Claim 1, wherein the nematic liquid crystal material is a mixture (in equal weight ratio) of *p*-anisylidene-*p*-*n*-heptyl-aniline, *p*-ethoxybenzylidene-*p*-*n*-butylaniline and *p*-*n*-propoxybenzylidene-*p*-*n*-pentylaniline.

3. A liquid crystal display device including the liquid crystal display material claimed in claim 1, said material being interposed between two glass substrate plates, the internal surface of each plate being covered at least in part with a thin film electrode at least one electrode being transparent and any remaining internal plate surface having no electrode being subjected to chemical cleaning treatment or being provided with an electrically insulating vacuum evaporated film.

4. A liquid crystal display device according to claim 3, wherein the transparent thin film electrode is formed of an electroconductive layer containing an oxide of tin, titanium, indium or cadmium.

5. A liquid crystal display device according to claim 3, wherein the electrode is formed of Al, Ni, Pd, Ag or Au.

6. A liquid crystal display device according to claim 3, wherein the electrically insulating evaporated film is formed of magnesium fluoride, silicon oxide, aluminium oxide, barium oxide, beryllium oxide, bismuth oxide, magnesium oxide, nickel oxide, antimony oxide, tellurium oxide, thorium oxide, zinc oxide, indium oxide or tin oxide.

7. A liquid crystal display material or a device containing same according to claim 1 or claim 3 respectively, substantially as hereinbefore described with reference to Fig. 1, or Figs. 2 and 3 of the drawings and the experimental Example or Examples 1 to 3.

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FIG. 1

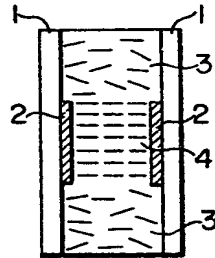


FIG. 2

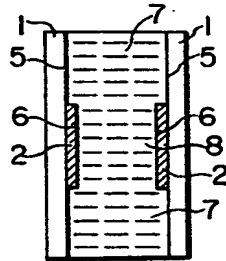


FIG. 3

